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Task Order 0039: Topologically Constrained Networks in Metallic Glasses

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14. ABSTRACT
This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at Wright-Patterson AFB, Ohio from 18 July 2005 through 29 September 2005. The research applied concepts associated with the Topologically Constrained Network (TCN) model to perform evaluations of the Dense Cluster Packing (DCP) model for metallic glasses. The effort demonstrated that the ABC model has good potential for predicting bulk metallic glass compositions. The model is technologically very useful because all the information needed to calculate glass forming compositions in a system is already available through phase diagrams and crystal structure tables.

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1.0 INTRODUCTION

Bulk metallic glasses have unique technological properties much different than corresponding crystalline alloys of the same composition. Examples are high yield strength and high corrosion resistance. Further, being glassy, they can be formed easily into complex shapes. This combination of desirable engineering properties makes metallic glasses extremely attractive to Air Force Systems.

While many metallic compositions have been made in the glassy state, the search for bulk metallic glass compositions in technologically important systems remains at present largely an empirical exercise requiring large effort and time. There exists a need to develop a fundamental understanding of why certain compositions form glasses easily (i.e., have good glass forming ability, GFA).

Several approaches have been proposed in the literature to rationalize the relationship between GFA and the alloy composition. These approaches can be classified as:

a) Macroscopic: These attempt either to correlate GFA with some measurable property or to estimate the critical cooling rate – the minimum cooling rate necessary to form a glass of some specified thickness (say 1 mm) - as a function of composition using macroscopic thermodynamics and kinetics.

b) Microscopic: These attempt to rationalize, at an atomic level, the kinetic sluggishness of the glassy state to crystallize. For example, Miracle at AFRL [1] has developed a dense cluster packing model based on a prescribed connection of solute centered dense clusters.

The goal of the present work was to apply to metallic glass systems a different microscopic approach, which is based on the average bond-constraint density. We will refer to this model as the ABC model. In the ABC model, the structure of a glass is viewed as an extended topologically - disordered (TD) network of rigid atomic bonds with an energy comparable to that of the corresponding equilibrium crystalline state. The basic ideas of the ABC model have been worked out in detail for ionic and covalent systems [2, 3]. This report evaluates the potential of the ABC model for predicting glass forming compositions in metallic systems.

2.0 THE AVERAGE BOND CONSTRAINT (ABC) MODEL

2.1 Basic Principles

The ABC model is based on the following postulates:

1. The structure of a glass is a *3-dimensional network of rigid bonds* such that:
   a) The short range order (SRO) – defined by the set of near neighbor coordination numbers and distances – in the glass network of a given composition is the same as in the primary crystal phase for that composition.
   b) The glass network has no long range order and the network is topologically disordered (TD).

2. The stability of a glass network against crystallization is caused by:
   a) Low energy of the TD network
      i) The chemical energy of the network (determined by primarily by its SRO) is comparable to that of the crystal, and
      ii) The strain energy in the glassy network (i.e., the excess energy in bonds due to their lengths being different from the corresponding equilibrium lengths) is minimized.
   b) Crystallization requires rearrangement of topological disorder which is a process with high activation energy.

2.2 General Steps in Applying the ABC Model

1) The compositions and SRO's of the primary crystal phase are determined from the equilibrium phase diagram of the system and from the crystal structure tables.
2) An expression is formulated for the average number (n) of bond-constraints per atom in terms of the alloy composition (x), the bond strengths (weak or strong), and the SRO (the set of coordination numbers, Zij).
3) The degrees of freedom, f, per atom, defined as follows

   $f(x) \equiv 3 - n(x),$ (1)

   are calculated as a function of x.

Compositions for which f is negative, are termed over-constrained, have too much strain energy), and do not form a glassy network easily. When f is positive and large, the system is too flexible (or floppy) and permits rapid crystallization. A glass forms most easily at the composition X* for which

$$f(X^*) = 0 \qquad (2)$$

2.3 ABC Model Equations for a general binary system $A_{(1-x)}\ B_x$

An expression for the average bond constraint per atom, n(x), can be written as

$$n(x) = (1-x)\ \Theta_{AA}\ Z_{AA}/2 + x\ [\Theta_{BA}\ Z_{BA}+\Theta_{BB}\ Z_{BB}/2] + \mu_A\ (1-x)\ (2\ Z_A - 3) + \mu_B\ x\ (2\ Z_B - 3) \quad (3)$$

Here,

Θ_{ij} = relative strength of an average i-j bond (= 1 if strong , = 0 if weak).

$Z_{ij}\ (x)$ = coordination number of j atoms around an i-th atom.

$Z_i\ (x)$ = total coordination number of i-th atom.

μ_i = weight of the angular (covalent) bonds around the i -th atom.

X = mole fraction of the solute (i.e., component B).

While not shown explicitely in eqn 3, the coordination numbers in general vary with the composition. Using equations 1 and 3 and establishing Z_{ij} (X) from information

about the SRO of the primary crystal, one could calculate f(x) and, in turn, identify the values of X*.

In the case of a non-covalent ($\mu_A = 0$, and $\mu_B = 0$) binary system which exhibits large negative heat of mixing, it is reasonable to assume that $\Theta_{AA} = 0$, $\Theta_{BB} = 0$, and $\Theta_{AB} = 1$. For this case, eqn (3) reduces to

$$f(x) = 3 - xZ_{BA} \qquad (4)$$

Before solving for X* using eqn 4, it is necessary to establish the X-dependence of the coordination number, Z_{BA}.

2.4 Model for the Composition Dependence of the Coordination Numbers

For all compositions lying between two neighboring eutectic compositions Xeu(1) and Xeu(2), the primary crystal phase is the same. According to the ABC model, the SRO in the melt is identical to the SRO of the primary crystal when the composition of the melt is same as that of the crystal. When the two compositions are different, we postulate that

a) The environment around all solute atoms in the melt is the same as in the primary crystal. This implies that the coordination numbers Z_{BA} and Z_{BB} are constant and equal to their respective values in the primary crystal.

b) The total coordination number of A (i.e., $Z_A = Z_{AB} + Z_{AA}$) is also the same as in the primary crystal. Since Z_{AB} is determined from the equality:

$$Z_{AB} = [X/(1-X)]\ Z_{BA} \qquad (5),$$

it follows that

$$Z_{AA}(X) = Z_A(\text{Total}) - Z_{AB}(X). \qquad (6)$$

2.5 Application to the Ni-Nb System

The following data about crystalline and eutectic compositions and SROs are available from phase diagrams [4] and crystal structure tables [5] in the Ni-Nb system:

Crystal #	X(Crystal)	X(Eutectic)	Z_{AA}	Z_{AB}	Z_{BA}	Z_{BB}
1 (FCC Ni)	0	0.16	12	0	12	0
2 Ni_3Nb	0.25	0.41	8	4	12	0
3 Ni_6Nb_7	0.54		8	8	7	5
4 (BCC Nb)	1.00		0	8	0	8

Using this SRO information and eqns 5 and 6, we can now write the expressions for the x dependence of Z_{ij}. These expressions are shown in Table II.

Table II; Expressions for coordination umbers in the Ni-Nb system.

Composition Range	Z_{AA} (X)	Z_{AB}(X)	Z_{BA}	Z_{BB}
X < 0.16	12 (1-2X)/(1-X)	12X/(1-X)	12	0
0.16 - 0.41	12(1-2X)/(1-X)	12X/(1-X)	12	0
0.41 – 0.54	(16-23X)/(1-X)	7X/(1-X)	7	5
0.54 – 1.00	8	0	0	8

Using Eqn 4 and the values of Z_{BA} shown in table II, it can be shown that X* can take only two values: 0.25 and 3/7 (= 0.43). The value X = 0.25 corresponds to the intermetallic compound Ni_3Nb with high liquidus temperature and thus is not suitable glass forming composition. This leaves X = 0.43 as the only composition suitable for forming glasses in the Ni-Nb system.

3.0 DISCUSSION

Before discussing the result for the Ni-Nb system, it is useful to emphasize the following about the ABC model.

a) While, in principle, the ABC model provides a method for calculating X* values, these compositions only represent relatively easy glass forming compositions. Glasses can always be formed for any composition provided the melt is cooled sufficiently rapidly.

b) The calculated values of X* are only approximate as the calculations depend on various assumptions about the bond strengths, covalency, and coordination numbers. Clearly, calculated value of X* points to a small composition range where glass formation may be easy. One could estimate this composition range (X_1* to X_2*) from the following equations:

$$X_1^* = 2.5/ Z_{BA} \quad \text{and} \quad X_2^* = 3.5 / Z_{BA}. \qquad (7).$$

c) Lastly, additional information such as liquidus temperature, eutectic and intermetallic compound compositions should be complemented to the calculated X* values when finalizing the best glass forming compositions.

For the Ni-Nb system, the composition range for X* corresponds to 0.43 ± 0.07 (i.e., 0.36 to 0.50). The actual data [6,7] in the Ni-Nb system show that good glass formation occurs at several compositions 0.37, 0,44, 0.50, and 0.60. The first three are all within the predicted range. This good agreement provides a strong support for the ABC model for calculating the glass forming composition range.

4.0 CONCLUSIONS

This work has demonstrated that the ABC model has good potential for predicting bulk metallic glass compositions. The model is technologically very useful because all the information needed to calculate glass forming compositions in a system is already available through phase diagrams and crystal structure tables.

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